

# Characterisation of pulverised fuel ash derived from coal and biomass co-firing and their utilisation into value added products

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## ABSTRACT

Pulverised fuel ash (PFA) has been marketed for a long time as a cement extender, when its residual carbon or loss-on-ignition (LOI) content is consistently below 7wt. %. Strategies to reduce NO<sub>x</sub> emissions have resulted in an increase in the concentration of unburned carbon in the fly ash (i.e. LOI > 7 wt. %), and therefore restricting its use in the cement industry. Moreover, the marketability of fly ash is further complicated by the increasing use of alternative fuels, like biomass and import coals. This paper describes the characterisation of four fly ashes derived from coal and one fly ash sample derived from biomass co-firing with coal. All these samples were collected from different power plants and derived from different fuels.

## KEYWORDS:

PFA, alternative fuels, ash utilisation, beneficiation

## 1. INTRODUCTION

The burning of fossil fuels in industrial power stations plays a significant role in the production of electricity. Modern thermal power plants produce large amounts of solid waste, including PFA (pulverised fuel ash), typically 8-10% by mass of fuel. PFA had been marketed for a long time as a cement extender, when its residual carbon or loss-on-ignition (LOI) content is consistently below 7wt. %. Strategies to reduce NO<sub>x</sub> emissions have resulted in an increase in the concentration of unburned carbon in the fly ash (i.e. LOI > 7 wt. %), and therefore, restricting its use in the cement industry [1]. This has limited the principal use of the inorganic ash in the cement industry, since the unburned carbon tends to adsorb the air-entrainment agents, which are added to the cement to prevent crack formation and propagation. Moreover, the marketability of fly ash is further complicated by the increasing use of alternative fuels, like biomass and import coals.

Power plants can co-fire of biomass fuels with coal up to 6%. Biomass fuels exhibit more variation in composition of inorganic material compared to coal, as they can vary from woody to herbaceous and other resources [2]. Various types of biomass produce ash that has similar pozzolanic activity as coal fly ash, which include rice husk, wheat straw, sugar cane straw and wood [3,4]. The aim of this work is to identify applications for high carbon fly ashes derived from coal and their comparison to a biomass-co-firing ash.

## 2. EXPERIMENTAL WORK

Five fly ash samples were received from different power plants and derived from different fuels. Table 1 shows the list of the samples, power plant, and the collection device. Only sample B1 was derived from co-firing of biomass (5% oat) and the rest of the samples are derived from import coals. The B3, B4, and B5 samples were collected from power plant 3 and were sampled from front to back rows of the precipitator.

Table 1: Fly ash samples used in this work.

Samples	Power plant/Fuel type	Collection device
B1	1 / 5% biomass (Oat)+Coal (Russian)	Economiser
B2	2 / Coal (La Loma; Colombia)	Mechanical separator
B3	3 / Coal (Pittsburgh; US)	Electrostatic Precipitator
B4	3 / Coal (Pittsburgh; US)	Electrostatic Precipitator
B5	3 / Coal (Pittsburgh; US)	Electrostatic Precipitator

### 2.1 Loss-on-ignition (LOI)

The loss-on-ignition (LOI) for the samples was determined according to the ASTM C311 procedure using a SDT-TGA 600 [5]. Around 1g of sample was oxidized in air for 3 hours at 805 °C to constant weight in a muffle furnace. The LOI content was then calculated from the weight loss of the sample after oxidation and corrected for moisture content. The LOI analyses were conducted in duplicate.

### 2.2 Beneficiation via incipient fluidisation

Incipient fluidisation process was selected for the fly ash beneficiation of high carbon fly ashes. The apparatus used is presented in Figure 1.

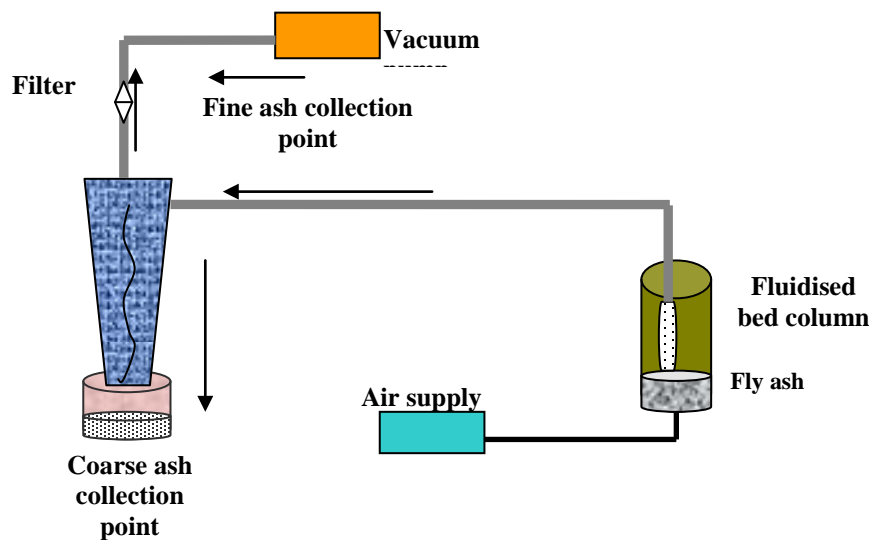


Figure 1: Incipient fluidisation process for fly ash beneficiation.

For this work, incipient fluidisation has been preferred as it is a dry separation method which does not expose the carbon to potential contaminants that may alter its reactivity or properties. Additionally, a sieving process was applied for each stream in order to improve the separation, by removing fine material that is difficult to separate with incipient fluidisation. This technique segregates carbon rich particles from mineral-rich particles on

the basis of density. The height of the fluidised bed column, shown in Figure 1, is 28.5 cm. The inside diameter is 3 cm. The height of the fly ash bed ranged from 2-5 cm. Air is introduced from the air supply at the bottom of the fluidised bed. The flow rate should be low in order to generate laminar particle motion, while avoiding the large-scale bed flows that lead to macro-mixing and homogenisation of the sample. Capillary suction removes the bubbling particles and feed them into a cyclone filter, where the coarse carbon rich particles fell down into a vessel. The finer particles are removed from the top of the cyclone and collected in a special filter that prevents the particles from blocking the vacuum pump. Finally, the vacuum pump pulls the floated particles into the cyclone filter.

### 2.3 Carbon activation

The activation system used for the steam activation is presented in Figure 2. The main part is the horizontal furnace. Typically 2-3 g of sample was placed inside the horizontal tube furnace in a silica boat. The distance from the entry part into the furnace to the silica boat is 450 mm. Nitrogen gas was firstly passed at 150 ml/min to achieve an inert atmosphere. After 30 minutes, the furnace was heated to the desired activation temperature under a flow of nitrogen gas in terms of inert atmosphere. A thermocouple was used to monitor the furnace temperature. When the sample reached the desire activation temperature, a flow of deionised water was introduced into the furnace at 8 ml/min to generate steam for the activation. The water flow was introduced by gravitational force as the water reservoir was kept at a higher level than the furnace. The steam was swept through the furnace by the flow of nitrogen. During the activation, liquid and gas products were swept from the tube outlet into the liquid collector (vessel) as shown in Figure 2. After a certain activation period, the feeding water into the furnace was stopped and the heating was shut off, except N<sub>2</sub> gas feed to prevent any oxidation occurs and cool it down.

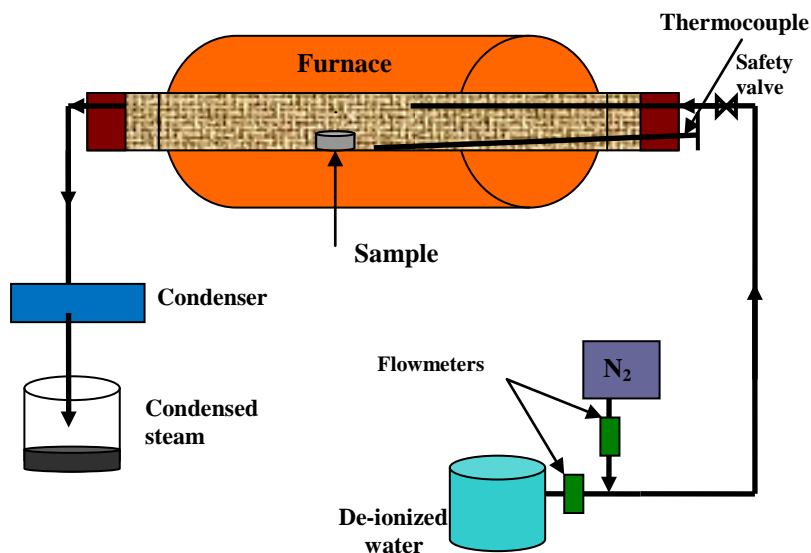


Figure 2: Schematic diagram of steam activation system.

## 2.4 Cement tests

Two fly ashes were chosen for air entrainment agent test B1, and B2. B1 and B2 samples were mixed with the cement at a 10 % wt. Typically, six cubes of 100 mm were prepared for each mixture. The mix details of each cube are shown in Table 2. The coarse and fine aggregates were procured from Trent valley gravel. The air entrainment agent (AEA) used was AE3 Cormix. The cubes were prepared to do compression strength tests for 7 days and 28 days.

Table 2: Mixing details of each cube for 5% and 10% Cement+PFA.

Material	Kg-(10%-mixture) for B1 and B2 samples
Cement	1.7
Coarse aggregates	6.86
Fine aggregates	6.3
PFA	0.189
H <sub>2</sub> O	1400 ml
AEA	9.5 ml

## 3. RESULTS AND DISCUSSION

### 3.1 LOI analysis

The LOI values are presented in Table 3. B1 and B2 samples presented lower LOI values compared with B3, B4, and B5. The error of these measurements is  $\pm 5\%$ .

For the B3, B4, and B5 samples collected from front to back rows of the precipitator, the LOI values increase going from the front to back rows of the precipitator (Table 3). LOI variations between hoppers have been previously reported for fly ash samples [6], where fly ashes from hot-side hoppers presented lower LOI values than those derived from cool-side hoppers. This “hot-side” and “cool-side” terminology has been adopted from former studies and it is based on characteristics of the respective ashes, where fly ashes from hot-side collectors present characteristics associated with higher temperatures (lower carbon content) compared to those of their cool-side counterparts [6]. These samples were intentionally selected for this work due to their high LOI values (Table 3) and therefore being suitable to conduct fly ash beneficiation.

### 3.2 Incipient fluidisation

Incipient fluidisation was applied on all these samples. Table 3 shows the LOI values for parent fly ash samples and the beneficiation products. The experimental error is  $\pm 8\%$ .

Table 3: LOI values before and after beneficiation process for all the samples studied.

Sample	Parent	Low-carbon product		High-carbon product	
	LOI (wt.%)	LOI (wt.%)	Yield %	LOI (wt.%)	Yield %
B1	8.1	4.0	49.4	60.5	50.6
B2	12.1	1.5	12.4	81.5	87.6
B3	15.5	5.3	34.2	37.2	65.8
B4	20.4	8.5	41.7	40.2	58.3
B5	35.7	11.7	32.8	55.2	67.2

It can be seen that B1, B2, and B3 present lower LOI value for low-carbon stream than the acceptable level of 7% wt. [5,7] and high LOI values for the high-carbon stream. In contrast, B4 and B5 samples present higher LOI value for the low-carbon stream than the acceptable

level. This suggests that samples B4 and B5 need multi stages to obtain a good separation. Particle size distribution studies of these samples are being conducted to understand the effect of the particle size in the separation yields obtained. .

### 3.3 Carbon activation

This method was conducted for the high-carbon stream samples produced from the fly ash beneficiation. Figure 3 shows the BET surface areas of the activated carbons and solid yields. The carbon activation was carried out by steam at temperature 850°C for 60, 90 and 120 minutes for all the samples studied. The surface areas throughout this work are presented on carbon basis, which was calculated by dividing the surface area after activation obtained from the BET measurement by carbon content. The error of the surface areas is in the range of  $\pm 3\%$ , including the error from the activation process by running duplicates and surface area analyses process by measuring duplicates using the BET method.

The solid yields are relatively high since the fly ash carbon has already undergone devolatilization in the combustor [9]. As expected, the solid yield is decreases with activation time for all the samples, where the largest decrease in solid yield was observed after two hours activation. This behaviour has also been reported for the activation of anthracites [10] and bituminous coals [11].

The B1, B2, B3 and B4 samples present a significant increase in the surface area going from one to two hours activation compared with B5 sample that shows a decrease in surface area after two hours activation (Figure 3). During activation, the B1 biomass co-firing sample follows similar trend to the fly ashes derived from coal in terms of presenting a maximum with increasing solid yields (Figure 3). However, in contrast to the coal derived ashes, the biomass co-firing sample reaches higher surface areas at higher carbon yields.

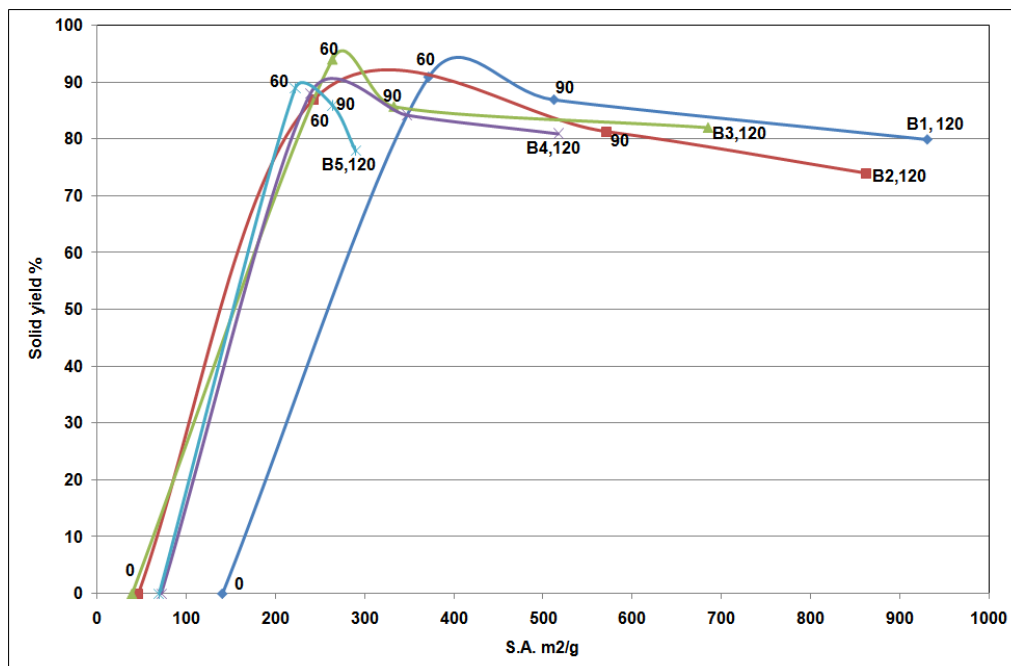


Figure 3: Solid yield and BET surface areas (carbon basis) for the fly ash carbons activated with steam for periods of 60, 90 and 120 minutes.

### 3.4 Air entrainment agent (AEA) tests

For this work, three low-carbon ashes (Section 3.2) were mixed with cement as well as air entrainment agents (AEA) as described in section 2.4. The workability (i.e. slump) values for the samples prepared are shown in Table 4. The slump value for the B2 sample was higher than for the B1 sample (130 vs 50 mm). Scanning electron microscopy (SEM) studies conducted on these samples (not presented here) have shown that that B2 has more spherical particles than B1, and therefore it needs less water for preparing the cement admixture. The B1 biomass co-firing sample presents more non spherical particles, which can reduce the workability of this sample. Therefore, the water required for this mixture (i.e. biomass co-firing + cement) had to be measured carefully in order to get better workability (e.g. recommended value around 70 mm) [12]. This is consistent with previous work that has reported that biomass co-firing PFA particles are irregular in shape, have higher porosity, and higher in LOI value than coal derived ashes [13,3].

Table 4: Cement tests for concrete specimens at 7 days test for three low carbon ash streams.

Sample Mixture	Slump (mm)	Max Load (KN)	Compressive strength (N/mm <sup>2</sup> )	Mass in air (Kg)	Mass in water (Kg)	Density (Kg/m <sup>3</sup> )
B1 (10% admixture)	50	156	15.5	2.2	1.2	2180
B2 (10% admixture)	130	93	9.3	2.1	1.1	2060

The results from the 7 days test are presented in Table 4 and it can be seen that the compressive strengths reported are very different, considering that the error is  $\pm 3\%$ . It is known that the compressive strength depends on the amount of cement, age of the cement, type of the cement used, water content, air content, amount of the PFA, density of the specimen, and the type of the agent. For a commercial sample for road base applications, the compressive strength value should be above  $30 \text{ Nm}^{-2}$ , while the compressive strength for light concrete is around  $16 \text{ Nm}^{-2}$  [14].

The density of the mixtures was measured at 7 days and is also presented in Table 4. It can be seen that the B2 mixture has the lowest density ( $2060 \text{ kgm}^{-3}$ ), compared with B1 mixture ( $2180 \text{ kgm}^{-3}$ ). The reason is because air voids inside the concrete specimens are less abundant for B1 compared with B2. However, the amount of water + AEA was higher in the B2 mixture (i.e. slump test shows a high value of 130 mm) compared to the B1 sample, indicating that B1 requires more water to prepare the cement mixture [15].

## 4. CONCLUSIONS

A series of five samples including one biomass co-firing from different power plants was selected due to their high LOI value. These samples were beneficiated physically using incipient fluidisation process to produce high and low-carbon streams for carbon activation studies and cement tests, respectively.

A one-step steam activation process was used to develop activated carbons from the carbon rich streams. It was observed that extended activation times increased the surface area of the activated carbon produced at the expense of the solid yield.

The biomass co-firing sample presented a lower water demand than the coal derived fly ash mixture. Moreover, biomass fly ash does not impact concrete setting behaviour and it can have useful applications for light weight concrete.

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